Vacancy-Impurity Nanoclusters in Solid Solutions ^{3}He $-^4$He

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The existence of vacancy–impurity clusters due to quantum properties of vacancies in phase separated solid solutions of ^{4}He in ^{3}He is analyzed and discussed. Additional mechanism called vacancy assisted nucleation is proposed. According to this assumption the vacancy-impurity clusters should have b.c.c. structure.

I. INTRODUCTION

Vacancy-impurity clusters (VIC) were predicted in 1978 by this author [1] (see also Refs. 2, 3) as one of a series structural effects that could appear due to the quantum nature of vacancies and impurities in quantum crystals. This effect was confirmed in 2001 [4] and further investigated [5, 6, 7] in the famous experiments of the Kharkov group, using new methods based on a precise measuring of the pressure variations in phase separation of solid solutions ^{3}He $-^4$He. The effect is based on the fact that the delocalization of a vacancy in a quantum solid is attended with a lowering of the energy by an amount of the half vacancion band width. This requires, however, a good periodicity of the surrounding area. In helium solid solutions the periodicity can be violated by isotope impurities. Hence, the vacancy could i) push out the impurities, ii) attract them and create a cluster of impurity atoms, or iii) rearrange host atoms and impurities in a periodic lattice. We shaw that all three possibilities can be realized in the helium solutions. Other possibilities can be found in Refs. 2, 3. Ganshin et al. [4, 5, 6, 7] observed clusters of ^{4}He impurities around vacancies in dilute solutions of ^{4}He in ^{3}He. They called them Andreev–Pushkarov nanoclusters having probably in mind some analogy between the structural effect in solid solutions and the magnetic vacancy in pure ^{3}He proposed by Andreev [8] but unfortunately not observed yet.

The aim of this article is to consider some peculiarities of the vacancy-impurity clusters and turn attention to an additional mechanism in their creation.

II. THE RID EFFECT

Let us consider an isolated vacancy in a dilute solution. Let ε_0 be the formation energy of a localized vacancy. The delocalization lowers this energy by an amount of $\Delta/2$ where Δ is the vacancion energy band width. Since

this is only possible in a periodic lattice, the impurities should be removed from a region of radius R (measured in this work in interatomic distances $a = (V_m/N_A)^{1/3}$). Due to the Heisenberg uncertainty principle the lowest energy level in such a potential region is approximately

$$\varepsilon = \pi^2\hbar^2/MR^2 = \pi^2 A/R^2 \qquad (1)$$

where we used the relation between the vacancion effective mass M and the tunnelling amplitude A for cubic crystals $M = \hbar^2/(Aa^2)$ with the interatomic distance $a = 1$. In the same notation the band width is $\Delta = zA$, z being the number of the nearest neighbours (for a h.c.p. lattice $M = \hbar^2/(2Aa^2)$, and the energy band consists of two partially overlapping parts [2, 3, 9]). The ridding changes the entropy. Hence, the change of the free energy is of the form

$$F = E - TS = \varepsilon_0 - \frac{\Delta}{2} + \frac{\pi^2 A}{R^2} + \frac{4}{3}\pi R^3 TS \qquad (2)$$

where $S = x\ln(e/x)$ is the entropy per unit lattice site, and x is the impurity concentration. Expression (2) has a minimum at [1]

$$R = \left(\frac{\pi A}{2TS}\right)^{1/5} \qquad (3)$$

and the volume of the rid region is

$$V_0 = \frac{4}{3}\pi \left(\frac{\pi A}{2TS}\right)^{3/5} \qquad (4)$$

This result is restricted by the requirement that the free energy be not smaller than $\varepsilon_0 - \Delta/2$, as well as by the condition $R > a$. The latter condition is stronger, and reads $TS < A$. In addition, the energy of the first quantum level (1) should be less than $\Delta/2$.

Of course, expressions (2) - (4) are only estimations showing the order of magnitude. These formulae do not take into account the change of the impurity concentration in the solution. The important result is that the size of the rid region is determined by the interplay between the amplitude A (the vacancy exchange integral, not the band width) and the entropy term and does not depend on the "won" energy due to the delocalization, $\Delta/2$, and the impuriton characteristics. The quantum nature of

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the impuritons shows itself in their mobility. The large value of the entropy term is the reason the zone motion of defects in ^{3}He to be suppressed.

Analogous formula has been obtained by Andreev [8] for the number of aligned spins N_s around a vacancy in solid ^{3}He. In that case $S = n \ln 2 = \ln 2$ and the expression (4) takes the form

$$N_s = \frac{4}{3}\pi \left(\frac{\pi A}{2T \ln 2} \right)^{3/5} \qquad (5)$$

This equation with $T = 150\,\text{mK}$ and $A = 1\,\text{K}$ yields $R \approx 1.5$ and $N_s \approx 14$. Note that with this value of R the delocalization energy $\pi^2 A/R^2 \approx 4.5\,\text{K}$ turns out to be larger than the half band width $\Delta/2$ in ^{3}He, i.e. the first quantum level does not lie in the well. The minimum value of the free energy turns out to be higher than the formation energy of a localaized vacancy: $F_{min} = \varepsilon_0 - \Delta/2 + 11.85\,A^{3/5}T^{2/5} \rightarrow \varepsilon_0 - \Delta/2 + 5.55 > \varepsilon_0$. Therefore, the effect considered should take place eventually in materials with very large bandwidths, but hardly in ^{3}He.

Let us turn back to the solid solutions ^{4}He $-$ ^{3}He. The approximation above can be improved [2, 3] for the more realistic case of vacancies in a solutiowith a given small concentration $x_v = n_v/N$ and a concentration of impurities $x = n_i/N$. As a result of ridding, the impurity concentration increases to the value

$$x' = \frac{n_i}{N - N x_v V} = \frac{x}{1 - x_v V} \qquad (6)$$

where V is the rid area around a vacancy. The problem can be formulated as looking for the minimal work for changing the concentration in the solution $x \rightarrow x'$ by removing $x_v V N$ particles of the solvent.

The Gibbs potential for a solution with concentration x is of the form [10]

$$\Phi_1 = N\mu_0 + NxT \ln \frac{x}{e} + Nx\psi \qquad (7)$$

where μ_0 is the chemical potential of a pure solvent, and $\psi = \psi(T, P)$.

After ridding the impurity concentration becomes x', since the same number impurities is distributed over $N' = N - x_v V N = N(1 - x_v V) = Nx'/x$ lattice sites. Therefore, the Gibbs potential $\tilde{\Phi}_2$ of the solution has the same form (7) with x and N replaced by x' and $N' = Nx'/x$, while the potential of the pure solvent removed is $\Phi_0 = x_v V N \mu_0$. Their sum is

$$\Phi_2 = \tilde{\Phi}_2 + \Phi_0 = N\mu_0 + NxT \ln \frac{x'}{e} + Nx\psi \qquad (8)$$

The difference $\Phi_2 - \Phi_1$ is

$$\Delta\Phi = NTx \ln \frac{x'}{x} \qquad (9)$$

Hence, the variation of the entropy equals

$$\Delta S = Nx \ln \frac{x'}{x} \qquad (10)$$

The change in the energy due to the presence of Nx_v vacancions in the system is

$$\Delta E = Nx_v \left(\varepsilon_0 - \frac{\Delta}{2} + \frac{\pi^2 A}{R^2} \right) \qquad (11)$$

and finally the free energy per particle takes the form

$$F = x_v \left(\varepsilon_0 - \frac{\Delta}{2} + \frac{\pi^2 A}{R^2} \right) - xT \ln \left(1 - x_v \frac{4}{3}\pi R^3 \right) \quad (12)$$

The free energy F has its minimum at [2, 3]

$$R = \left(\frac{\pi A}{2Tx'} \right)^{1/5}, \quad V_0 = \frac{4}{3}\pi \left(\frac{\pi A}{2Tx'} \right)^{3/5} \qquad (13)$$

In (13) the concentration x' stands instead of the entropy $S = x \ln(e/x)$. The minimal value of the free energy is then

$$F_{min} = \varepsilon_0 - \frac{\Delta}{2} + \frac{10}{3}\pi \left(\frac{\pi A}{2} \right)^{3/5} (Tx)^{2/5}$$

$$= \varepsilon_0 - \frac{\Delta}{2} + \frac{5}{2}n_x \qquad (14)$$

where $n_x = xV$ is the number of impurities rid by one vacancy. The change in the free energy affects the equilibrium vacancy concentration:

$$x_v = \exp \left\{ -\frac{\varepsilon_0 - \Delta/2}{T} - \frac{10\pi}{3} \left(\frac{\pi A}{2T} \right)^{3/5} x^{2/5} \right\}$$

$$= \bar{x}_v \exp \left\{ -\frac{5}{2}Vx \right\}. \qquad (15)$$

Hence, the equilibrium vacancy concentration decreases with increasing number of defects removed.

Let us evaluate the volumes V_0 and V for the typical values $A = 1\,\text{K}$, $T = 0.1\,\text{K}$, and $x = 1$ %. Then one has by means of eqs. (4) and (13) $V_0 = 123$, $V = 346$. For $T = 0.2\,\text{K}$ and $x = 2$ % the same expressions yield $V_0 = 60$ and $V = 150$ (we did not take into account an eventual dependence of x' on T). The dependence of the number of atoms in a cluster on temperature (at constant x') corresponding to formulae (4) and (13) are shown in Fig. 1. In fact, the number of the removed impurities by a vacancy $n_x = xV \sim 2 \div 5$ and the relative change of the concentration $\delta x/x$ is of the order of several percents. However, this can lead to a noticeable decreasing of the vacancy equilibrium concentration by more than 2 orders of magnitude (see eq. (15)). It is worth noting that the region considered is not a cluster. It consists of solvent atoms and has no boundaries, surface energy etc.

III. DIFFUSION

The ridding effect may be considered as an effective repulsion which prevents impurities and vacancies be closer
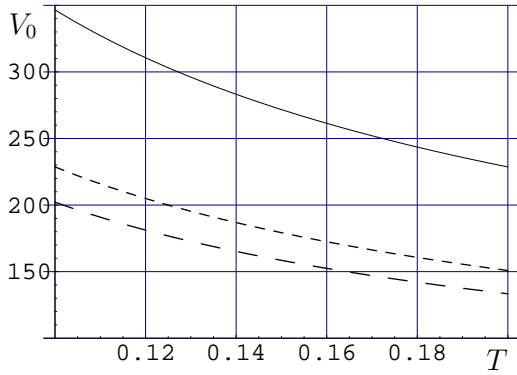
FIG. 1: The number of atoms V_0 as versus temperature at different concentrations. solid line: $x' = 1\%$ eq. (13), dashed line: $x' = 2\%$ eq. (13), long-dashed line: $x' = 2\%$ eq. (4).

to each other. This means that an effective cross-section of impuriton scattering on vacancies can be introduced. It can be evaluated by means of the radius R and is of the order of $\sigma \sim \pi R^2 \sim \pi (\pi A/2Tx)^{2/5}$. In order to avoid any misunderstanding we would like to note that this is not the case of ^{4}He impurities in ^{3}He, because their zone motion is embarrassed by the chaotic orientation of the nuclear spins of the lattice atoms. It could take place in a strong orienting magnetic field. The values of σ for a hypothetic quasiparticle in a medium with helium characteristics are $\sigma \sim 60\,a^2$ (at $T = 100$ mK and $x = 1\%$). The temperature and concentration dependencies of the diffusion coefficient in this case are

$$D = D_0 \frac{T^{2/5}}{x^{3/5}} \qquad (16)$$

We considered till now concentrations less than the saturation concentration x_s. If $x' > x_s$ then a new phase of impurities appears. The effect of vacancies on this phase is considered in the next section.

IV.   VACANCY-IMPURITY CLUSTERS

Let us consider a solid solution of impurity atoms (say ^{4}He) with a concentration $x = n/N$ where N is the number of solvent atoms (say ^{3}He). If $x < x_s$, Gibbs potential is of the form (7)

$$\Phi_1 = N\mu_0 + nT \ln \frac{n}{Ne} + n\psi \qquad (17)$$

where μ_0 refers to the pure solvent and $\psi = \psi(P, T)$. The chemical potentials μ_3 and μ_4 that correspond to the solvent atoms and impurities in the solution are

$$\mu_3 = \mu_0 - Tx, \quad \mu_4 = T \ln x + \psi \qquad (18)$$

Let us move δn impurities from the solution to their "pure" concentrated phase. The change of the thermodynamic potential is

$$\Delta\Phi = -\delta n(T \ln x + \psi) + \delta n\mu_4^0$$

The chemical potential μ_4^0 of the pure phase corresponds to some saturation concentration, x_s (otherwise, the phase should solve). Hence, $\mu_4^0 = T \ln x_s + \psi$, and

$$\Delta\Phi = -\delta n T \ln \frac{x}{x_s} = -NT\delta x \ln \frac{x}{x_s}. \qquad (19)$$

We suppose that all δn atoms are confined to n_v vacancies. Then, repeating the procedure in Sec. II yields

$$R = \left(\frac{\pi A}{2T|\ln(x/x_s)|} \right)^{1/5} \qquad (20)$$

with the restrictions $T|\ln(x/x_s)| < A$ and $x \neq x_s$. If the concentration x equals the saturation (equilibrium) concentration then the entropy term vanishes and the vacancy is fully delocalized. This effect should be seen in a rapid increase of the vacancy mobility inside the pure phase. Such an observation was reported in [11] where fast nonphonon excitations were found in solid ^{4}He with a small concentration of ^{3}He. Let us mention that x is the concentration in the matrix after the clusters are formed. The values of x and x_s should be taken from the experiment and the phase diagram. A quite sophisticated analysis using known data for helium solutions was recently made in Ref. [7]. The authors found for the cluster size $R \approx 2.1 \div 4.4$ a. A small correction to these values could appear if the band width Δ in the expression for the localization energy $\pi^2\Delta/R^2$ is replaced by A (see eq. (1)). Otherwise, the first quantum level ϵ turns out to lie out of the potential well with a depth $\Delta/2$ ($\pi^2\Delta/R^2 > \Delta/2$ for all values of R obtained).

For a rough evaluation one can simplify (20). If the initial concentration is x_0, then $x = x_0 - x_v V - n_s/N \approx x_s - x_v V$ where n_s is the number of atoms in the pure phase and we neglect the small number of solvent atoms solved in the pure phase. The initial concentration drops out as it should be in a case of phase separated mixture in equilibrium. Then (20) can be rewritten in the form

$$\frac{\pi A}{2T} = R^5 \ln\left| \left(1 - \frac{x_v}{x_s}\frac{4}{3}\pi R^3\right) \right| \approx \frac{x_v}{x_s}\frac{4}{3}\pi R^8 \qquad (21)$$

and therefore,

$$R = \left(\frac{3A}{8T}\frac{x_s}{x_v} \right)^{1/8} \qquad (22)$$

For $T = 150$ mK, $x_v = 10^{-5}$, $x_s = 5 \times 10^{-3}$ one has $R \approx 2.5$ and $V \approx 60$ ($x_v V/x_s = 0.12 \ll 1$). Unfortunately this approximation requires $x_v V \ll x_s$ and is not applicable to the most interesting low temperature case where x_s can be smaller than $x_v V$.

It is worth noting, that VIC can appear both inside an existing phase and as a separate inclusion. This makes difficult to evaluate the role of the surface energy.

V. LOCAL PHASE STRATIFICATION EFFECT, VACANCY ASSISTED NUCLEATION

This effect was predicted in the same work [1] (see Refs. [2, 3] as well) and is another indication for the quantum nature of vacancies. It appears when the vacancion band widths in two phases of one and the same substance (e.g. h.c.p. and b.c.c. ^{4}He) differ significantly. Let the h.c.p. phase be the stable one (near the transition to b.c.c.). If a vacancy appears, the energy increases by $\epsilon_h - \Delta_h/2$ (subscript h corresponds to h.c.p.). If it were in a b.c.c. phase, the energy change would be $\epsilon_b - \Delta_b/2$. Since near the phase separation the thermodynamic potentials of the pure phases are almost equal, the more favorable state is determined by the difference $\delta E = \epsilon_h - \Delta_h/2 - (\epsilon_b - \Delta_b/2) = \delta\epsilon + (\Delta_b - \Delta_h)/2$. For large enough Δ_b the difference $\delta E > 0$ independently of the sign of $\delta\epsilon$ and the b.c.c. phase with a vacancy has lower energy. Of course, the bottom of the band may become lower due to the large difference of the vacancy formation energies, but this seems not to be the case of helium crystals. The vacancy will rearrange the ^{4}He atoms from h.c.p. to b.c.c. hence creating a nuclei of a new phase. The size R of the nuclei can we evaluated using the procedure applied above. The difference of the free energy is

$$\delta F = \delta\epsilon + \frac{\pi^2 A}{R^2} + T\delta S \frac{4}{3}\pi R^3 \qquad (23)$$

where A is the vacancion exchange integral in the b.c.c. crystal. Having in mind that $T\delta S = q$ is the latent heat, one obtains the nuclei radius

$$R_n = \left(\frac{\pi A}{2q}\right)^{1/5} \qquad (24)$$

Let us note, that the surface energy in this case is smaller than in the case when the matrix and the nuclei have different structure (b.c.c. and h.c.p.). We were not able to find reliable data for the latent heat at the temperature region considered. If one takes $\Delta S \sim 10^{-2}$ extrapolating [12] then $q \sim 10^{-3}$ and $R_n \approx 4.4$, $V_n \approx 350$. These are probably the clusters observed in the experiments of Kharkov group. After the inclusion of ^{4}He with a vacancy appears, a local phase transition to the more favorable b.c.c. phase is performed. This makes the VIC even more stable. We suppose, that this effect could contribute to the curious observation in [13] that the lattice constants in both phases of a phase separated solution increase after heating.

Experimental evidences to support our hypothesis should be looked for not only in a phase separated solutions. As we showed in [1, 2, 3] inclusions of b.c.c. ^{4}He should manifest themselves in a hysteresis at b.c.c.-h.c.p. transitions of pure ^{4}He. In this case one can use the experimental data for the transition line h.c.p.-b.c.c. and a nuclei contains $\sim 200 \div 250$ atoms. Phase nuclei of the same kind and of approximately the same size should appear in the liquid helium near the liquid-solid transition line.

The theory of VIC is instructive from another point of view as well. At the first glance, the small exchange integral in spin-spin interaction of ^{3}He atoms compared to the vacancion bandwidth should lead to their easy orientation. It does not happen due to the large entropy factor. So, vacancy prefers to rearrange atoms (not spins) organizing a local phase of impurities and to delocalize in this phase. Its choice is the minimal change of entropy.

VI. CONCLUSION

In this work three effects due to the quantum nature of vacancies in solid helium were considered relative to the vacancy-impurity complexes observed recently in phase separated solid solutions of ^{4}He in ^{3}He. The size of a cluster depends on the ratio of the vacancy exchange integral A and the entropy term $T\Delta S$, and does not depend directly on the vacancion band width. The experimental results cannot give, therefore, information about the band width. Nevertheless, it is essential for the phase transition. It is supposed that VIC in rear ^{4}He - ^{3}He solutions undergo two transitions: first complexes with h.c.p. structure appear and then they transfer to b.c.c. clusters. The transition is controlled by the positions of the bottoms of the vacancy bands, and by the minimum entropy change. The evaluation of the clusters size is in good agreement with the experimental observations. It is shown, that near the separation line the size of the vacancy cluster rapidly increases, the vacancy becomes delocalized and mobil inside the ^{4}He- phase. It is supposed that this could be the fast nonphonon mode observed in [11]. The effect of vacancy assisted local phase stratification should be observable near the b.c.c.-h.c.p. as well as b.c.c.-liquid transition.

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